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NONTRADITIONAL RAW MATERIALS IN THE PRODUCTION OF ALUMINOSILICATE CERAMICS

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Promising nontraditional raw materials for aluminosilicate ceramics are considered: porcelain stones, in particular, quartz-sericite porcelain stone, kaolin from the Zhuravlinyi Log deposit, and complex additives represented by magnesium-bearing minerals (talc, marble, diopside, dolomite).

The use of nontraditional components in the production of aluminosilicate ceramics (porcelain, faience, etc.) is becoming increasingly topical.

Traditional natural minerals commonly used as raw materials are feldspars, clay, kaolin, quartz sand, and other mineral rocks.

However, extensive research results and practice of ceramic factories show an increasing use of nontraditional raw components, including porcelain stone, kaolins from newly prospected and developed deposits, diopside-bearing rocks, etc.

Porcelain stones belong to the class of promising nontraditional materials for ceramic production. Porcelain stones are regarded as products of hydrothermal-metasomatic transformation (kaolinization, ceritization, pyrophyllization, or chloritizing) of acid or, less frequently, medium effusive and subvolcanic rocks that have a fine-grained structure, a low content of pigment oxides, and a chemical-mineralogical composition making it possible to use them as the main component in ceramic mixtures intended for producing aluminosilicate ceramics.

According to specifics of porcelain technology, four main mineral types of quartz-bearing porcelain stones are distinguished [1, 2]: kaolin-quartz, muscovite-quartz, pyrophyllite-quartz, and feldspar-quartz (or quartz-feldspar).

The known varieties of porcelain stone as a rule exist in the form of associations of three or four rock-forming minerals. In determining the possibility of using porcelain stones of a certain mineral type in the production of aluminosilicate ceramics, their correspondence with the following requirements is usually taken into account: a sufficiently low content of colorant oxides ($Fe_2O_3 + TiO_2$) below 1% (here and elsewhere mass content is indicated); for higher grades this content should be below 0.6% and a sufficiently high total content of alkali metal oxides ($K_2O + Na_2O$). Based on the latter parameter, porcelain stones are subdivided into the following three varieties: alkali-free ($R_2O < 0.6\%$), normal alkalinity ($R_2O = 0.6 – 3.0\%$), and alkaline ($R_2O > 3.0\%$).

Based on the potassium modulus value, porcelain stones are classified as high-potassium ($K_2O : Na_2O > 3.0$), potassium-sodium ($K_2O : Na_2O = 3.0 – 1.0$), and sodium ($K_2O : Na_2O < 1.0$).

In Russia there is only one industrially mined deposit of quartz-feldspar porcelain stones, namely, the Gusevskoe deposit [2] in the Primorskii Region (the Far East). The rocks of this deposit are represented by hydrothermally modified rhyolites classified as the alkali type. The content of alkali metal oxides in these rocks is 6.78 – 9.08% with an insufficiently high potassium modulus.

Porcelain stones from other deposits located in the CIS have found limited application in the production of aluminosilicate ceramics.

Considering the need for expanding sources for ceramic materials, porcelain stones of the Dzhany-Dzhol'skoe deposit (Kirghizstan) located in the Uchkurt River valley are of interest. Porcelain stones of Kirghizstan are mineral rocks of white, gray, or pinkish color, highly textured, with detrital structural elements extended in one direction.

The main mineral of porcelain stone from this deposit is represented by detrital grains without visually identifiable inclusions. The refraction index is approximately 1.540. Microcline grains are found in an insignificant quantity and scales of mica-muscovite (sericite) are found in substantial quantities.

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TABLE 1

Sample	Mass content, %					
	quartz	kaolinite	sericite (muscovite)	anorthite	albite	other minerals
TP-1	67.00	3.00	22.00	2.50	5.00	1.01
TP-4	68.00	2.10	21.00	2.60	4.90	0.87
TP-5	65.91	2.90	25.90	2.40	4.02	0.91
TP-6	65.87	3.00	25.00	2.40	4.10	0.98
KTP-1	64.31	0.50	33.98	–	0.05	0.92
KTP-9	65.73	–	30.93	0.02	0.72	2.63
KTV-1	64.60	0.52	30.71	0.65	1.94	1.56
KTV-2	64.87	0.16	29.55	1.53	1.86	2.07
KTPS-1	66.07	1.48	27.32	1.28	2.91	1.00

The content of iron and titanium oxides ranges from 0.09 to 1.90%, the content of alkali metal oxides is low (on the average about 3.6%) with a stable prevalence of potassium oxide over sodium oxide ($K_2O : Na_2O = 3.3 : 0.4$).

The mineral composition of samples of porcelain stone from the Dzhany-Dzhol'skoe deposit is shown in Table 1.

The results of an integrated thermographic study of porcelain stone recorded two clear endothermic effects. The first one at 575°C of low intensity is accompanied by expansion of the sample and corresponds to the polymorphic transformation of β-quartz into α-quartz; the second one at 1150°C is related to decomposition of muscovite (sericite). The weight loss due to moisture removal starts at a temperature of 80°C and proceeds continuously at a constant rate up to 905°C, then the course of the curve of weight loss versus temperature becomes stabilized. Variations in the weight and size of the sample in heating reflect the process of dehydration of mica and kaolinite that make part of porcelain stone in a particularly finely disperse spate. Both these minerals contain water in interlayer spaces of the crystalline lattice, and removal of water in heating is accompanied by an increase in the sample volume due to expansion of the interlayer space. Thus, the behavior of porcelain stone belonging to quartz-muscovite rocks heated in the low-temperature range (up to 680°C) is mainly determined by fine-grained quartz present in a prevailing quantity, and in the higher-temperature range is determined by fine-grained muscovite and kaolinite.

The chemicomineral composition of quartz-sericite porcelain stone determines its specific behavior in firing and differences in the physicomechanical properties of aluminosilicate ceramics based on this stone from the properties of ceramics based on traditional materials. Analysis of the properties and phase composition of porcelain stone samples fired at different temperatures indicated that sintering of this rock starts at a temperature of 1250°C. The apparent density of samples fired at 1320°C reaches a maximum value at zero water absorption. A further increase in firing temperatures is accompanied by a decrease in its apparent density, presumably due to the formation of sealed porosity.

Analysis of the results of quantitative x-ray phase analysis indicates that mullite starts crystallizing in porcelain stone samples in firing up to 1200°C, and the quantity of mullite does not grow while the firing temperature increases to 1410°C and remains equal to 9%.

At the same time, dissolution of quartz grains is registered in the temperature range of 1200 – 1250°C, and the quantity of quartz decreases with increasing firing temperature. The results of electron microscope analysis of porcelain stone samples fired in a temperature range of 1200 – 1400°C reveal there structural modifications depending on firing temperature. Thus, the structure of samples fired at a temperature below 1200°C is heterogeneous. It is represented by quartz grain of size from 1.5 – 2.0 to 10 μm or more and needle-shaped mullite crystals, whose sizes reach 1 μm. Large quartz crystals are not always clearly visible; they seem to be concealed by a vitreous phase, and round bubbles sized up to 1 μm are visible in some of them. Possibly these are gaseous-vitreous inclusions. Between quartz crystals one can see clearly defines sites (around 8 μm) filled with drops of an irregular shape that are apparently formed from the liquid phase, which at the next stage of the process serves as a basis for mullite crystallization from the muscovite melt.

As the firing temperature of samples grows to 1250 and 1280°C, no substantial changes in the sizes of quartz and mullite crystals are observed. However, the zone of quartz grain fusion perceptibly increases and at the same time the quantity and sizes of gaseous-vitreous inclusions decreases.

The structure of samples fired at 1350°C and 1410°C have significant similarity. The main crystalline phases are quartz and mullite. The contours of quartz grains acquire a rounded shape, and their fusion zone grows to 4 μm. At the same time, growth of mullite crystals within the limits of muscovite pseudomorphoses is registered. The mullite crystals are short-prismatic, frequently of a rounded or nearly square shape. Twin crystals seemingly split in half are found as well. The size of mullite crystals is 0.5 – 1.0 μm. Some mullite crystals have round openings, whose diameter is around 0.1 μm.

The quantity of quartz in samples of quartz-sericite porcelain stone fired at 1410°C due to dissolution decreases from 67 to 37%, the gaseous-vitreous inclusions disappear (within a temperature interval of 1250 – 1280°C), and fluid vitreous melt liquates into two liquids, one of which is the matrix and the other one forms drops in it.

Sintering of the porcelain system starts at a temperature of 1150°C, i.e., from the moment registered as the start of shrinkage, and ends at 1320°C, which corresponds to zero water absorption, maximum apparent density, and relatively low linear shrinkage.

In sintering of quartz-sericite porcelain stone there is intense crystallization of mullite and cristobalite, and quartz grains dissolve in the surrounding melt, which forms a vitreous phase in cooling. Mullite crystals observed along the borders of mineral grains, as a rule, have a needle-shaped

habitus, and mica (muscovite) grains have short-columnar habitus with no bridges registered along their axes. All the above processes occurring in thermal treatment of quartz-sericite porcelain stone were manifested in sintering of aluminosilicate ceramics based on it.

It can be expected that porcelain stones will be subsequently used as one of the main components in the production of aluminosilcate ceramics.

During the past decade kaolin from the Zhuravlinyi Log deposit (Chelyabinsk Region) was widely and successfully tested at several factories as the main plastic component in production of aluminosilicate ceramics. Data on its physicochemical properties and the results of using this kaolin in ceramic mixtures for various purposes are described in detail in the scientific literature [3]. It should be noted that the use of this nontraditional plastic component not only eliminated the dependence of Russian ceramic manufacturers on kaolin supplies from Ukraine, in particular, kaolin from the Prosyanovskoe deposit, but also stimulated research intended to stabilize structural-mechanical properties of slips and improve the physicotechnical properties of ceramic materials.

In implementing the results of this research it was observed, first, that in order to stabilize properties of ceramic suspensions, it is advisable to introduce kaolins from different deposits with different granulometric and mineral compositions; second, stabilization and improvement of properties of ceramic mixtures can be accomplished by mechanical activation of plastic components and by introduction of various additives.

Note as well that extensive research carried out in the past decade has significantly expanded the concept of the effect of nontraditional components, which can be regarded as a complex-effect additives, on structure and properties of ceramics [4 – 7].

Among the minerals most frequently reported as effective ones are oxides of magnesium, calcium zinc, lithium, and other chemical elements. These additives have a positive effect on improving whiteness and mechanical strength of aluminum oxide ceramics and on lowering its firing temperature. Moreover, the mineralizing effect of additives becomes more efficient if they are used as binary or ternary combinations. Consequently, natural magnesium-bearing minerals have been used as mineralizing additives, such as Onotskoe talc $3MgO \cdot SiO_2 \cdot H_2O$, Onotskoe magnetite $MgCO_3$, Slyudyanskoe wollastonite $CaO \cdot SiO_2$, marble $CaCO_3$, Slyudyanskoe diopside $CaO \cdot MgO \cdot 2SiO_2$, Zaigraevskoe dolomite $CaCO_3 \cdot MgCO_3$, etc.

The following factors are taken into account in selecting additives:

– the content of the set of oxides that have a positive effect on properties of aluminosilicate ceramics.

– the possibility of introducing this set of oxides via relatively inexpensive natural minerals that virtually do not contain colorant impurities;

– the effect of oxides integrating the additive on melt properties in firing;

– avoiding a negative effect on the properties of ceramic mixture in molding, etc.

As a consequence of introduction of complex additives into ceramic mixtures, a significant improvement of properties of aluminosilicate ceramics was accomplished and its competitiveness substantially increased.

The above directions of upgrading aluminosilicate ceramic technology appear quite topical, since their implementation significantly increases production efficiency.

REFERENCES

1. V. I. Magidovich and V. I. Fin’ko, “Porcelain stones,” in: *New Types of Nonmetallic Raw Materials* [in Russian], Nauka, Moscow (1975), pp. 46 – 61.
2. *Porcelain Stones of the USSR* [in Russian], Nedra, Moscow (1988).
3. G. N. Maslennikova, N. V. Kolyshkina, A. S. Shamrikov, and Z. V. Stafeeva, “Concentrated kaolin of Zhuravlinyi Log deposit for ceramic production,” *Steklo Keram.*, No. 1, 15 – 19 (2002).
4. G. N. Maslennikova, “Physicochemical processes of porcelain structure formation,” in: *Chemistry and Technology of Silicate High-Melting Nonmetallic Materials* [in Russian], Nauka, Leningrad (1989), pp.202 – 218.
5. G. N. Maslennikova and Yu. T. Platov, “The process of porcelain formation in the presence of additives,” *Steklo Keram.*, No. 2, 19 – 24 (1998).
6. I. Kh. Moroz, “Specifics of structure formation and atomistic aspect of interpretation of solid-phase reactions in porcelain,” *Steklo Keram.*, No. 5, 12 – 15 (1995).
7. V. I. Vereshchagin, V. V. Kozik, V. I. Syryamkin, et al., *Polyfunctional Inorganic Materials Based on Natural and Synthetic Compounds* [in Russian], Tomsk (2002).